Evaluation of Passive Samplers for Field Measurements of Ambient Ozone in the National Parks

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ABSTRACT

In 1993 a follow-up study was conducted to the 1991 trials by the National Park Service of passive samplers for integrated measurement of ozone. A preliminary factorial design study was used to verify consistency between samplers and between analysis laboratories. It was found the significant differences in measured ozone were being introduced by the polypropylene rain shields that were used in the 1991 trials. PVC plastic rainshields were used subsequently.

For the main part of the 1993 study, five sites in two different national parks were used to compare passive sampler ozone measurements to average hourly exposures determined with UV-photometric ozone analyzers. Passive sampler measurements agreed well for each site and were within ±10% accuracy for each measurement period. The overall collection factor varied somewhat by site (21.565 ±1.59 cm^3/min), had good repeatability at each site, but overall accuracy fo multiple sites was ±20%. The passive samplers generally met the criteria established prior to the study and appear to be suitable for field use to measure ambient ozone when used as part of a well designed ozone measurement program.

INTRODUCTION

Ambient air quality monitoring in remote locations such as national parks and wilderness areas using conventional instrumentation is hampered severely by the general lack of commercial AC power in these areas. Information on air quality levels in these areas is often necessary to address resource management issues related to the effects of air pollution on the natural resources of such areas.

Interest in personal exposure monitoring over recent years has resulted in the development of passive sampling devices that contain no moving parts and rely simply on the principle of gas diffusion. Although passive devices were designed initially to sample over durations of a few hours, they are now being tested over durations of a few weeks for use in ecological monitoring programs[1].

In 1991 a study was conducted by the National Park Service to evaluate the accuracy of the Ogawa passive ozone samplers during sampling durations of one week or longer under a variety of environmental and meteorological conditions. The passive samplers were deployed at eight NPS ozone monitoring locations with different average relative humidity, elevations, and ozone mixing ratios. Other variables, such as, temperature, winds, solar radiation, and site environment were also measured.

The conclusions of the 1991 study were that the accuracy exceeded ±20% , that larger numbers of replicates were needed, and that differences in collection rates between parks were unacceptably large. A linear relationship between passive and continuous ozone measurements was obtained with an R^2 of 0.40.

Short exposures (1 week) of the passive samplers worked better than extended (4 -12 weeks) exposures. In light of those results, a second, more limited study with specific objectives was proposed.

A number of other field trials of the passive ozone samplers have been reported,[1-5] however, several of these have not appeared in the peer review literature as yet. Prior reports on field use of the passive samplers have indicated an accuracy of ±20%, which is far from what is expected from a continuous ozone monitor. However, for areas where no ozone measurements are available, even the ±20% would be an improvement in the understanding of local ozone exposures.

EXPERIMENTAL

The 1993 study consisted of a preliminary experiment designed to resolve experimental problems that were noted in the 1991 trials and a main experiment designed to test accuracy, precision, and number of replicate samplers required. Multiple sites were chosen to test the variability of the passive samplers under field conditions.

The Ogawa passive samplers consist of a double-sided filter holder that is mounted on a “badge” with a clip on the back. Inside the filter holder are two nitrite coated filters. When the nitrite coated filters are exposed to the air, ozone diffuses through the end-caps and reacts with the nitrite to form nitrate. To protect the samplers from direct contact with water, a rainshield was made from 7.6 cm diameter PVC drain pipe, a PVC end-cap, and Teflon tubing for supports. The samplers are mounted so they are 1.3 cm about the open end of the rainshield.

A preliminary experiment was designed to study some of the variables that could effect passive samplers. A 2^3 factorial design was used to examine the effects of analysis by different labs, type of rain shield, and relative placement of the samplers within the rain shields. Eight combinations of the three factors were studied at a contractor’s facility. Analyses of the coated filters were performed in laboratories at the Harvard School of Public Health and at Research Triangle Institute (RTI). Thus, 10 samples went to each lab from this preliminary study.

The main study plan was conducted in August at three sites within Great Smoky Mountains NP and at two sites within Sequoia-Kings Canyon NP. At each site there was a continuous ozone monitor for local calibration of the passive samplers and enough replicates were used to ensure that differences of 5 ppb ozone would be statistically significant between sites. Each exposure consisted of 5 passive samplers and 2-4 blanks. This allowed for subtraction of the blank for each set of samples and an estimate of the limit of detection for the method. Analysis were based on composites of coated filters from the two sides of each Ogawa device. All samplers had the same coating levels of nitrite and used the same extraction volumes in the analysis. The passive sampler badges were mounted inside PVC rainshields and the rainshields hung from PVC supports attached either to the monitoring site shelter or tower. Each passive sampler was located at the same height as the continuous ozone monitor intake and within five feet of the intake.

The sites differed by elevation and vegetation, both of which were expected to affect ozone levels and local winds. Although the projected ozone concentrations at the two parks were expected to be similar, the organic precursors for the formation of the ozone were expected to differ. Sequoia-Kings Canyon NP would generally be expected to have larger anthropogenic concentrations of volatile organic compounds (VOC) and Great Smoky Mountains NP to have larger biogenic concentrations of VOC. This difference challenges the passive samples more than if adjacent parks were used for comparison.

RESULTS AND DISCUSSION

Results from the preliminary study aided in the planning of the main study. A significant finding was that the polypropylene rainshield used in the 1991 study led to ozone values 30% high. The PVC rainshield gave results comparable to published reports[2] and had greater reliability. The other factors of badge location and analysis lab were found to contribute less than 2% error.

The unexposed passive samplers, here referred to as blanks, provided the baseline amount of nitrate on the filter pads. In the 1991 study the average one-week exposure blank was 156 ppb-hrs whereas in the 1993 study the average blank was 538 ppb-hrs. In general the blank analysis at RTI was consistent for the different weeks and about one-half the nitrate observed by the Harvard lab. The higher blanks obtained by the Harvard lab may be because they were analyzed a few weeks later or may indicate some analytical bias. The limit of detection (LOD), taken as three times the standard deviation of the blanks, was calculated as 1.5 ppb average ozone exposure over one week.

Reproducibility for the passive samplers was determined from the replicates. To remove the influence of different ozone levels, the relative standard deviation (RSD) was calculated as the percent where the standard deviation was divided by the average ozone mixing ratio. For the 1993 study, the RSD for the duplicates was 1.0% for Great Smoky Mountains NP (Table I) compared to the 5.0% in the 1991 study. At Sequoia-Kings Canyon NP, the present RSD was less than one-fifth of the value in the 1991 study. The lower variability was most likely due to use of the PVC rainshields, to use of a larger number of replicates over a shorter exposure time, and to improvements in the handling and analysis of the samples. An estimate for the precision (as the 95% confidence interval) of the passive was ±1.0 ppb. This was better than expected from the results in the previous study.

Since each field site had a continuous ozone analyzer collocated with the passive samplers, a collection factor was calculated for each site by sampling period. In principle the collection factor should not change either with week being sampled or the sample location. In practice the results indicate a shift in the collection factor from an as-yet-to-be-identified interference. Table II shows the changes in the collection factors by site during the study and Table III summaries the collection factors by week and park. Although the collection factors at Great Smoky Mountains NP suggests an elevation pattern (i.e., increasing collection factor with increasing elevation), the relationship does not hold for the samplers at Sequoia. It is likely that some influence other than atmospheric pressure is involved.

The best results were obtained when the average collection factor for multiple sites in one park were used for the samplers in that park. An overall collection factor of 21.565 ±1.59 cm^3/min (95% confidence limits) was used to compute the ozone exposures in the different parks. The 95% confidence limits for the collection factor were ±7.4% compared to ±12.1% for the 1991 study.

Direct comparison between the passive sampler and the continuous analyzer ozone concentrations are presented in Figure 1 for all of the sites and exposure periods. The linear regression line in Figure 1 is given as equation (1):

$$\text{Passive } O_3 = 0.963 \times (\text{Continuous Ozone}) \qquad R^2 = 0.91 \qquad (1)$$

This data set was not well suited for determining the response linearity of the passive samplers. However, as can be seen from Figure 1, all of the data falls within the ±20% values.

CONCLUSION

The results of this study indicate that the Ogawa passive ozone samplers can be used to measure ozone with an accuracy of better than ±20% and with enough precision to distinguish to better than 5 ppb between two sites within a park. The reproducibility of measurements is such that only 2 samplers need to be used at each measurement site to achieve this level of precision. Within these boundaries, the passive samplers appear to be suitable for low-cost spatial and temporal ozone measurements within a given park where there is a continuous ozone monitor to act as a reference.

With slightly less accuracy, the passive samplers can be used at widely separated parks when a common collection factor is used for the calculation of the ozone exposures. It is recommended that either a temporary continuous ozone monitor should be collocated with one of the sampling sites or the nearest existing ozone monitor should be used with collocated passive sampling as a check on the collection factor. The passive samplers can be used as screening devices for those locations where no prior ozone monitoring has taken place.

REFERENCES

1. Mulik, J. D., J. L. Varns, P. Koutrakis, M. Wolfson, D. Williams, W. Ellenson, and K. Kronmiller, "The Passive Sampling Device as A Simple Tool for Assessing Ecological Change," in *Proceedings of the 1991 U.S. EPA/A&WMA International Symposium on "Measurement of Toxic and Related Air Pollutants"*, **VIP-21**; Air & Waste Management Association: Pittsburgh, 1991; pp 285-290.

2. Koutrakis, P., J. Wolfson, A. Bunyaviroch, S. Froehlich, K. Hirano, and J. Mulik, "Measurement of Ambient Ozone Using a Nitrite-coated Filter," *Anal. Chem.*, **65**, 209-214 (1993).

3. Mulik, J. D., EPA, AREAL, "Study Shows Passive Sampling Devices Cost-effective Alternatives for Remote Monitoring," *EPA AMTIC News*, Vol. **3**, No. 3, p. 2, 1993

4. Helming, M., EPA, Region VIII, "An Ozone Saturation Study Along the Utah Wasatch Front," *EPA AMTIC News*, Vol. **3**, No. 3, p. 6, 1993

5. Schweiss, J., EPA Region X, "Method Development Study for an Inexpensive Portable Ozone Sampler," *EPA AMTIC News*, Vol. **3**, No. 3, p. 6, 1993.

Table I. Comparison of Passive Sampler Precision by Week and Site (ppb Ozone).

National Park	Individual Sites	First Week Std. Dev.	First Week Average Ozone	First Week RSD	Second Week Std. Dev.	Second Week Average Ozone	Second Week RSD
Great Smoky Mt.	Uplands	0.4	22.9	1.8%	0.7	23.5	3.1%
Great Smoky Mt.	Look Rock	0.8	58.0	1.3%	1.0	56.5	1.7%
Great Smoky Mt.	Cove Mt.	2.4	61.3	3.8%	0.8	58.2	1.4%
Sequoia-Kings Canyon	Lower Kaweah	--	--	--	0.6	74.0	0.8%
Sequoia-Kings Canyon	Grant Grove	--	--	--	0.4	67.3	0.6%

Table II. Calculated Collection Factors for Passive Samplers by Location (cm^3/min).

National Park	Individual Sites	Site Elevation (ft)	Week 1 Calculated Col. Factor	Week 2 Calculated Col. Factor	Average Col. Factor	Std. Dev.
Great Smoky Mt.	Uplands	2,000	19.07	18.75	18.91	0.16
Great Smoky Mt.	Look Rock	2,700	20.98	24.29	22.63	1.66
Great Smoky Mt.	Cove Mt.	4,100	24.12	26.86	25.49	1.37
Sequoia-Kings Canyon	Lower Kaweah	6,200	--	19.43	19.43	--
Sequoia-Kings Canyon	Grant Grove	6,600	--	20.82	20.82	--

Table III. Summary of Collection Factors by Week for Each Park (cm^3/min).

	Week 1 Great Smoky Mountains	Week 2 Great Smoky Mountains	Week 2 Sequoia -Kings Canyon
Average	21.39	23.30	20.13
Std. Dev.	2.08	3.39	0.70
Range	5.05	8.12	1.39

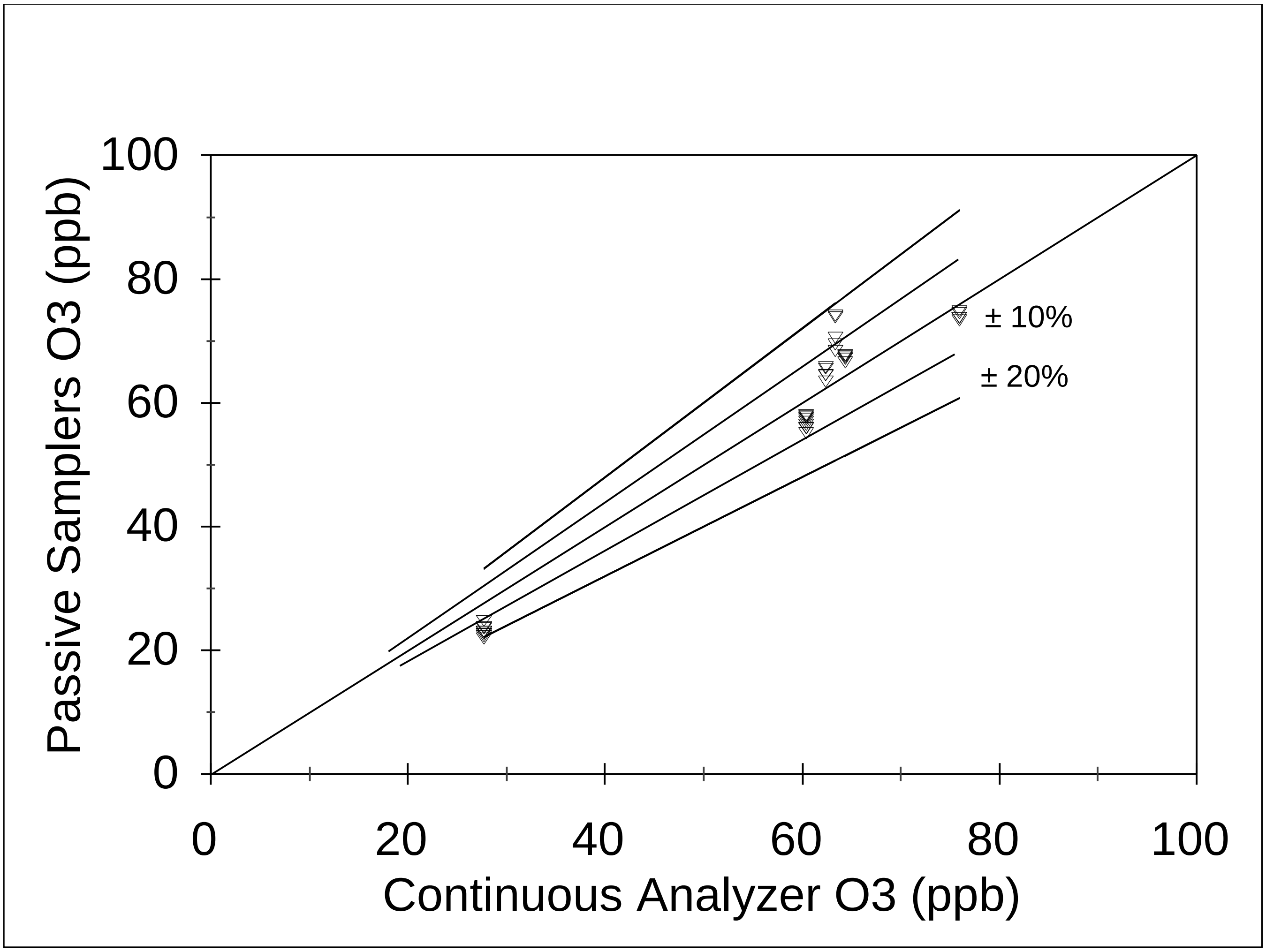

Figure 1. A comparison of continuous analyzer ozone and passive sampler results. The best fit regression line and ±10% and ±20% ranges are shown. Slope = 0.96, R^2 = 0.91